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TiO_2 immobilized PCL for photocatalytic removal of hexavalent chromium from water

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ABSTRACT

Photocatalytic remediation technologies employing titanium dioxide (TiO_2) particles have excellent applications due to the photoactive nature of this semiconductor. TiO_2 nanoparticle immobilization to polymer can be considered as alternative technique for the production of cheap materials for water remediation. The aim of this study is to produce an anatase type nano TiO_2 particles immobilized *into* or *onto* biodegradable polymer polycaprolactone (PCL), using simple solvent-cast processes. Produced materials were investigated and tested for photocatalytic reduction/removal of inorganic contaminant chromium(VI) ions from water. TiO_2 immobilized polymer successfully reduced/removed Cr(VI) ions (0.1–0.03 mM which is equal to 5–1.5 mg/L, respectively) from aqueous solution at pH 2 employing UV light (365 or 254 nm) source. Reduction of Cr(VI) ions to Cr(III) oxidation state was successful and the removal percentage was significantly high. TiO_2 immobilized *into* PCL (at 5% w/w) removed almost 40 ± 1% of Cr(VI) ions at 5 ppm initial concentration. Presence of citric acid as positive hole scavenger promoted the removal percentage and it reached to 96 ± 0.9% for 1.5 ppm initial concentration after 150 min exposure with 254 nm light source. Photocatalytic removal was still high as much as firs run for the second and third cycles (95 ± 1.5 and 89 ± 2% removal after a 150 min illumination, respectively). These results indicate that TiO_2 immobilized material can be reused for several times after a simple remediation process. Furthermore, the material can be simply damped into soil and left for total biodegradation if it lost its photocatalytic properties.

Keywords: Biodegradable polymer; Polycaprolactone; Photocatalytic removal of chromium (VI)

1. Introduction

Semiconductor photocatalysis is being considered as an alternative method for treating water polluted by various chemicals. Heterogeneous photocatalysis employing semiconductors such as TiO_2, CdS, ZnS or ZnO has demonstrated their efficiencies in removal of many pollutants by oxidative or inductive mechanism into relatively harmless end products. Apart from others, titanium dioxide (TiO_2) catalyst gained great interest due to its chemical stability and high reactivity. Fundamentally, mechanistically, and applications wise this technology has been already published by several groups [1–3].

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Formation of the holes (h^+),$^{\cdot}OH$ radicals, O_2^-, and H_2O_2 play important role in the reaction mechanism. TiO_2 photocatalyst is the source of both photocatalytic oxidative and reductive reactions which occur simultaneously on the particle surface (Eqs. (1)–(6)). Electrons produced by photo excitation are available for reduction of any species such as metal ions.

$$TiO_2\,(h\nu) \rightarrow e^- + h^+ \tag{1}$$

e^- reactions:

$$O_2 + 2e^- + 2H^+ \rightarrow H_2O_2 \tag{2}$$

$$H_2O_2 + e^- \rightarrow HO^{\cdot} + OH^- \tag{3}$$

$$H_2O_2 + h\nu \rightarrow 2HO^{\cdot} \tag{4}$$

h^+ reactions:

$$H_2O + h^+ \rightarrow HO^{\cdot} + H^+ \tag{5}$$

$$OH^- + h^+ \rightarrow HO^{\cdot} \tag{6}$$

Reducibility of a metal ion depends on its standard reduction potential. Potentials, more positive than 0.4 V, were required for reduction by TiO_2. It was suggested that the rates of oxidation (of organics) and reduction (of metals) were intrinsically interrelated to each other. Oxidants (i.e. metals or oxygen) promote the destruction of organics, whereas reductants (organics or water) were required for the reduction of metals [4]. Modified catalyst are prepared by doping TiO_2 with metals or nonmetals to promote oxidation. Alternatively, some hole scavengers (to scavenge the positive holes on TiO_2) are also used in reaction medium for effective reduction of the metals.

Photocatalytic reduction of hexavalent chromium ions, Cr(VI), with TiO_2 suspensions were studied by several groups and some recent studies [5–14] are given in Table 1.

The photocatalytic reduction of Cr(VI) ions in the presence of organic compounds as sacrificing agent increases the reduction rates [5,7–11,13]. Addition of citric acid in reaction medium has increased the reduction rate by more than 20 times, relative to the reduction of Cr(VI) alone [10]. Testa et al. report that [5] the addition of oxalate or ethylenediamine tetraacetic acid (EDTA) facilitate Cr(VI) reduction, inhibiting the electron-shuttle mechanism taking place in pure water at pH 2.

The particle size of TiO_2 is an important issue for an effective treatment since the surface area extremely increases with decreasing particle size. This leads to production of more oxidation and reduction sites. After a certain treatment period, solid TiO_2 particles should be separated from water and this process requires advanced and expensive filtration techniques. If the particle size is decreased to obtain higher removal efficiencies then this filtration step becomes more crucial. However, if TiO_2 nanoparticles are being stabilized *into* or *onto* a suitable material, the catalyst can be easily removed from the reaction medium. Nano sized TiO_2 particles can be immobilized on a suitable surface in the form of thin film. Glass, metal, and ceramic materials can be coated with a film layer using a proper coating technique. Most of these techniques require a high temperature calcination step for the stabilization of nanoparticles on surface. This calcination step is also required to obtain anatase crystal structure of TiO_2, which is a photoactive structure among TiO_2 crytals. Because of these drawbacks, thin film coating techniques are not suitable for mass production of TiO_2 containing polymeric materials. However, immobilization of TiO_2 nanoparticles directly *into* or *onto* polymer is a good alternative for production of photoactive materials.

Two important reviews were published that specifically concentrated on TiO_2 immobilized polymer substrates [15,16]. TiO_2 immobilized polymeric materials were used for photocatalytic removal of various organic pollutants, especially for removal of textile dyes. A very recent paper has been published by our group for effective removal of Cr(VI) ions from water involving Ag-TiO_2 incorporated poly styrene (PS) particles [17]. Addressing the above reasons, (problems at film coating and high temperature calcination step) TiO_2 nanoparticle coating/immobilization *into* or *onto* polymer can be considered as alternative technique for the production of cheap materials for remediation of chromium-polluted water. Direct immobilization of photocatalyst TiO_2 might be a logical alternative for easy and convenient immobilization [18]. Polycaprolactone (PCL) is a good candidate to prepare photocatalyst immobilized polymeric material since it is biocompatible, biodegradable, and nontoxic synthetic aliphatic polyester that undergoes complete degradation under attack of micro-organisms or enzyme [19,20]. Two routes can be employed, either dispersing the TiO_2 nanoparticles into the polymer or spraying onto polymer surface during casting process. Some applications of these procedures for the immobilization of TiO_2 *into* or *onto* polymers are available in the current literature [18,21–25]. In general, these reports usually discuss and evaluate the structural properties of polymer itself and

Table 1
Published studies related to photocatalytic removal of Cr(VI) ions with TiO_2

Catalyst	Conditions	Removal efficiency	Light source and type	Reference
TiO_2	• pH 2–3 (under air and N_2 atmosphere) • 41.6 ppm • Presence of CrO_4^{2-} or EDTA • 1 g/L	• No donor 52% (60 min) • 100% with oxalate (60 min) • 100% with EDTA (15 min)	Photo reactor, 400 W med. pressure halogen lamp	[5]
SO_4-TiO_2	• pH 2.5 • 40 ppm • 1 g/L catalyst	• 80% with TiO2 calcinated at 400°C (180 min) • 75% SO_4-TiO_2 calcinated at 500°C (180 min)	Photo reactor, 500 W high pressure mercury lamp	[6]
TiO_2	• pH 4 • 10 ppm • Presence of 10 ppm humic acid • 2.5 g/L catalyst	• 75% with TiO_2 (120 min) • 90% humic acid-TiO_2 (120 min)	Photo reactor, 2 × 15 W UV lamp, 365 nm	[7]
TiO_2	• pH 2 • 5–20 ppm • Presence of citric acid • 2.5 g/L catalyst	• 100% (2 h)	Sun light irradiated concentrating parabolic trough reactor	[8]
TiO_2	• pH 3 • 8.3 ppm • Presence of dibutyl phthalate (DBP) • 2.0 g/L catalyst	• 100% with TiO_2 (240 min) • 100% DBP-TiO2 (180 min)	• Photo reactor 350 nm UV	[9]
TiO_2	• pH 2 • 20.8 ppm • 1.0 g/L catalyst • Presence of organic species		• Photo reactor 20 W UV lamp, 254 nm	[10]
TiO_2	• Neutral-acidic pH • 20 ppm Cr(VI) • Presence of 20 ppm humic acid • 0.1–0.3 g/L catalyst	• 35% with TiO_2 (100 min)	• Photo reactor 65W UV lamp, 254 nm	[11]

(*Continued*)

Table 1 (*Continued*)

Catalyst	Conditions	Removal efficiency	Light source and type	Reference
TiO_2 electrode	• pH 3 • 28 ppm Cr(VI)	• 98% (at 64 rpm, 30 min)	• Rotating mesh type reactor 1,000 W UV lamp, 300 nm	[12]
WO_3 doped TiO_2 nanotubes	• 20 ppm • Presence of citric acid	• 50% with TiO_2 nanotubes (180 min) • 100% Wx-TiO_2 nanotubes (135 min)	Xe lamp, 100 mW/cm_2	[13]

usability of photocatalytic degradation of some organics. It should be noted that the direct adsorption of the pollutants by polymer itself also makes significant contribution to successful remediation.

The immobilization route of anatase nano TiO_2 particles *into* or *onto* polycaprolactone (PCL) employing solvent-cast processes has already been evaluated in details by our research group [18,25]. As an extension of previous studies, the utility of TiO_2 immobilized polycaprolactone for the photocatalytic removal or reduction of chromium (VI) ions in aqueous samples is designed in this study. Cr(VI) is mobile in the environment, highly toxic, and can easily penetrate the cell wall. It exerts its toxic influence in the cell itself, usually leading to various cancer diseases. We aimed the production of a cheap material for effective removal of Cr(VI) ions via its photo reduction to nontoxic Cr(III) as well as its removal by polymeric material.

2. Materials and methods

2.1. Preparation of TiO_2 immobilized PCL

Polycaprolactone pellets were used (CAPA® 6800, a mean molecular weight of 80.000 Perstop Caprolactones, Cheshire, UK) for preparation of the polymer. Analytical grade chloroform (Merck, Darmstadt) was used to dissolve the pellets for casting. For the immobilization of 44 nm sized TiO_2 powder (Aldrich, Darmstadt) *into* (defined as PCL-1) or *onto* (defined as PCL-2) polymer, two solvent casting techniques were used. Details of preparation and structural evaluation of the materials including the stability tests of PCL-1 and PCL-2 under UV irradiation have been given in our previous study [18].

2.2. Photocatalytic studies with PCL-1 and PCL-2

Removal studies were carried out for the photocatalytic reduction of aqueous solution of chromium(VI) ions. A series of experiments were designed to measure the adsorption of ions and compare the photocatalytic actions of the materials before and after exposure. All experiments were conducted at pH 2 since acidic pH was shown to be more effective in removal [5–10] and chromium ions were present in its Cr(VI) state at this pH [26].

The concentration of Cr(VI) ions was measured by diphenyl carbazide spectrophotometric method [27]. This method involves the formation of Cr(VI)-diphenylcarbazide complex at acidic condition. A linear calibration graph is obtained from the standard solutions between 0 and 5 ppm range. For this, 1 mL of diphenylcarbazide solution (250 mg dissolved in 250 mL acetone) was added to 10 mL standard solution in a 50 mL flask and diluted to the mark with distilled water. The flask was capped and mixed thoroughly by inverting the flasks several times. It was given minimum 10 min for full color development, and absorbance of each standard was measured at 540 nm. The same procedure was repeated for 5 mL portion of sample after appropriate dilution.

Photocatalytic processes require the adsorption of Cr(VI) ions on the polymer. Therefore, adsorption studies should be investigated in detail before photocatalytic treatment. Photocatalytic studies with PCL-1 or PCL-2 were carried out with different set of experiments. A 5 mL portion of aqueous Cr(VI) solution (containing 0.1–0.03 mM Cr(VI) ions) prepared from $K_2Cr_2O_7$ in double distilled water and a rectangular polymer specimens (each one approximately 2 × 1 cm and 0.08 g, approx. 0.5 mm thick) were placed in a quartz reaction cell. The pH of solution was adjusted with 0.1 M H_3PO_4 and the solution was illuminated with a UV lamp for photocatalytic treatment (Spectroline ENF-260, 2 × 8 W, producing 365 and 254 nm light). Sample was taken out from reaction vessel for measurement of remaining Cr(VI) ions during 60 min treatment period. The residual Cr(VI) concentration after a certain treatment period was determined and removal percentages were calculated from these data using the following equation:

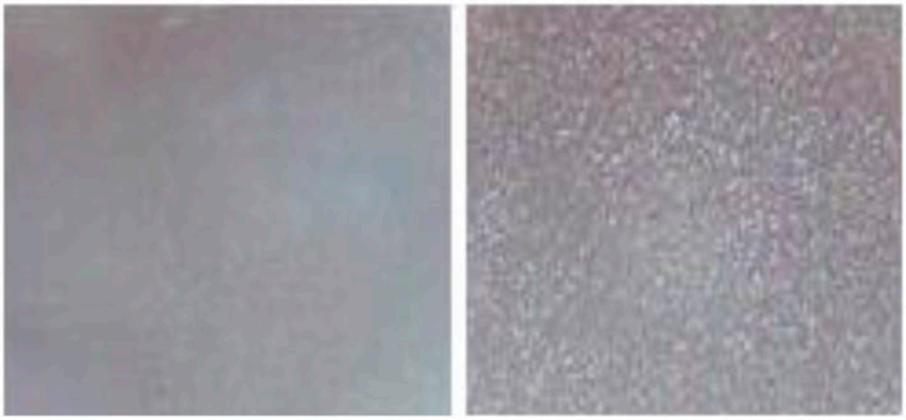

Fig. 1. Microscopic view of PCL-1 and PCL-2.

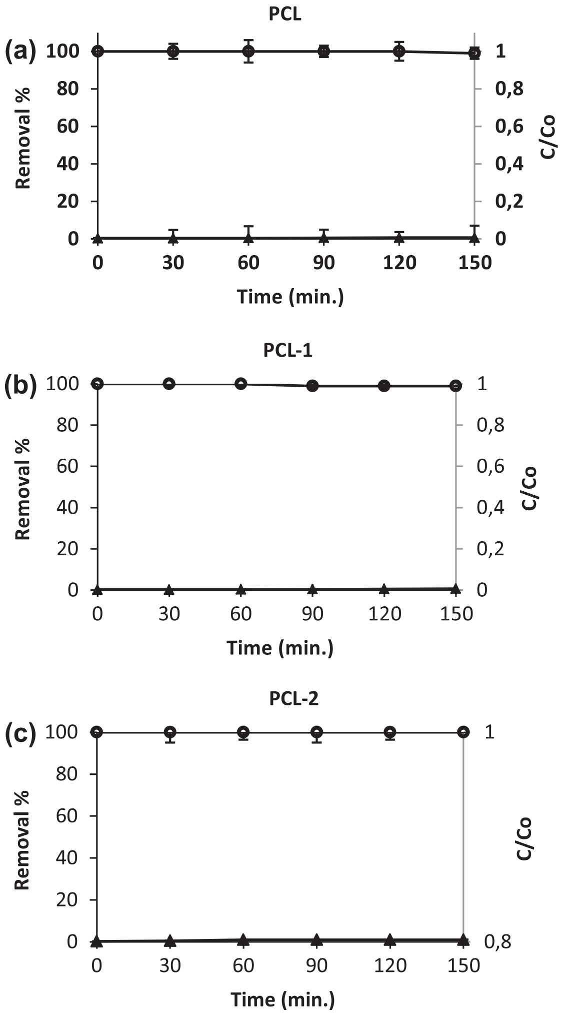

Fig. 2. Removal of Cr(VI) in dark with neat (a) PCL, (b) PCL-1, and (c) PCL-2 (initial concentration 5 ppm, solution volume 5 mL, polymer mass: 0.08 g, and pH 2), —o— C/Co, and —▲— Removal %.

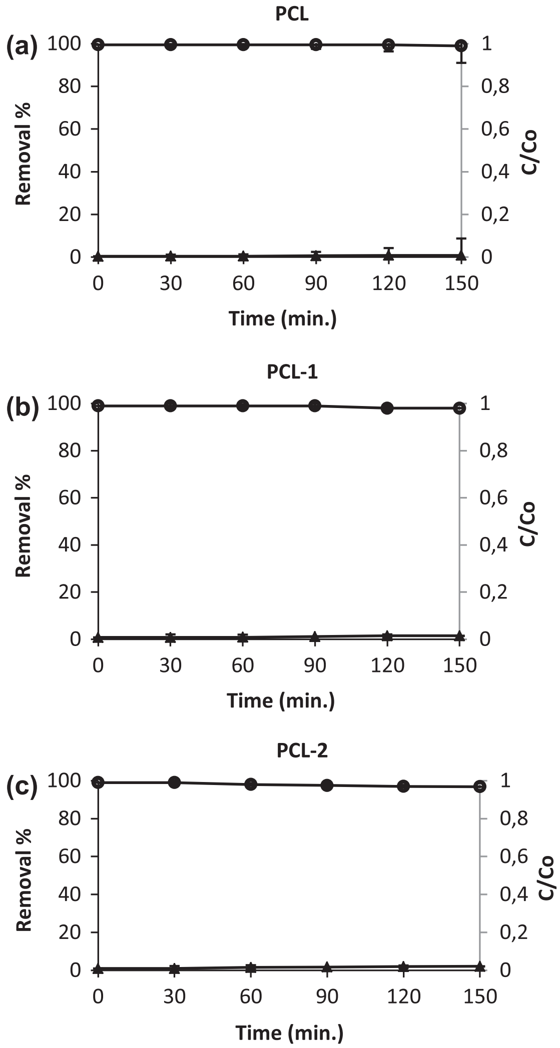

Fig. 3. Removal of Cr(VI) in dark with neat (a) PCL, (b) PCL-1, and (c) PCL-2 (initial concentration 1.5 ppm, solution volume 5 mL, polymer mass: 0.08 g, and pH 2) —o— C/Co, and —▲— Removal %.

$$\text{Removal }\% = \frac{[\mathrm{Cr(VI)}]_0 - [\mathrm{Cr(VI)}]_t}{[\mathrm{Cr(VI)}]_0} \times 100$$

Results were expressed as removal percentage before and after treatment, employing above equation. All experiments were carried out in triplicate.

2.3. Photocatalytic studies with neat TiO_2

Above experimental studies were also carried out in the presence of neat TiO_2. The amount of TiO_2 in 0.08 g of PCL-1 and PCL-2 was 0.004 g. Photocatalytic degradation of Cr(VI) solution (5 or 1.5 ppm, equal to 0.1–0.03 mM Cr(VI) ions) in neat TiO_2 suspension was compared to the results obtained with PCL-1 and PCL-2 using the same experimental set-up. Additionally, all studies were repeated in the presence of citric acid. This compound is used as sacrificial electron donor to scavenge the hydroxyl radicals and to deplete the positive holes (h^+) formed during photocatalytic process.

3. Results and discussion

Characteristic properties of materials were determined using sophisticated surface and structural analysis methods. Detailed information concerning the morphology of the polymeric materials (neat PCL, PCL-1, and PCL-2) before and after UV exposure can be found in our previous study [25]. It was confirmed that PCL did not undergo any major degradation for short period UV illumination (150 min for present study). Only long term UV exposure (1 week) caused slightly sheaf-like features as a result of oxidative damage. Due to uneven distribution and aggregation of nanoparticles, a non-homogenous material was obtained when TiO_2 immobilized *into* the polymer. However, spraying n-TiO_2 suspension using a spray gun *onto* partly solid PCL substrate produced more homogenous material (Fig. 1).

Although, TiO_2 particles were finely dispersed *into* the polymer aggregates were still clearly seen in some region. On the other hand, TiO_2 particles were evenly distributed *onto* the surface producing more homogenous surface.

3.1. Photocatalytic removal of Cr(VI) with TiO_2 immobilized PCL

Initially, the adsorption of Cr(VI) ions by polymer itself (PCL) was investigated in dark experiments. Therefore, studies were carried out by 5 and 1.5 ppm initial Cr(VI) concentrations in dark (given in Figs. 2 and 3, respectively).

Adsorption studies reveal that Cr(VI) is not removed by direct adsorption onto PCL, PLC-1, or PCL-2. Neat PCL or TiO_2 immobilized PCL seems to be not attractive for adsorption of Cr(VI) ions. In general, PCL itself is a good adsorbent for many chemicals since it has a non-uniform surface in the form of fused spherule-like aggregates. However, only small fractions of Cr(VI) ions were adsorbed by PCL (<2 ± 0.5%) for both concentrations indicating that adsorption was not favored by Cr(VI) ions at studied pH. The photocatalytic reactions provided better removal rates and the amount of Cr(VI) ions removed from reaction medium was significantly increased (see Fig. 4) especially at lower Cr(VI) concentration (1.5 ppm, Fig. 4(b)).

Photocatalytic studies revealed that 365 nm UVA light was not efficient for an effective removal even at 1.5 ppm Cr(VI) concentration. In Fig. 4(a), the removal efficiency of the PCL-2 in the 5.0 ppm

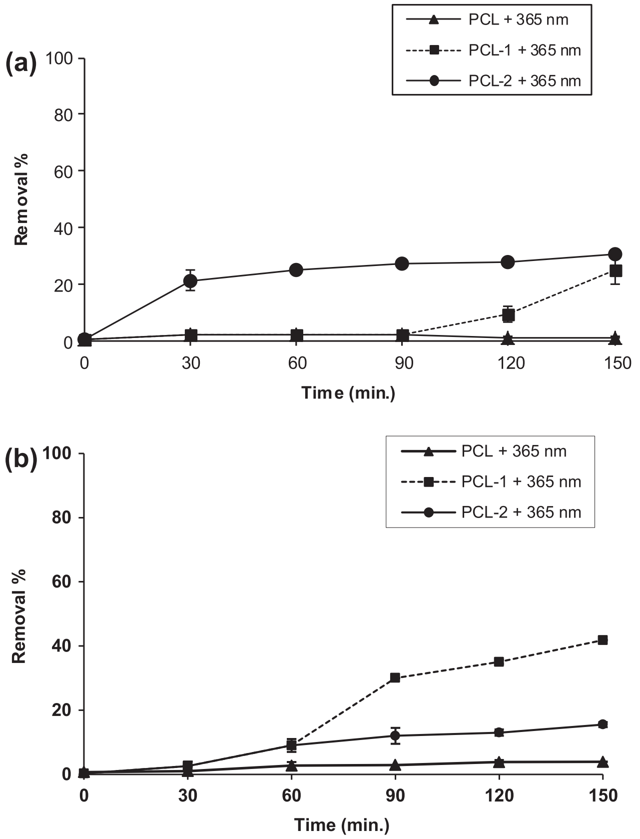

Fig. 4. Removal of Cr(VI) in presence of 365 nm light source with neat PCL, PCL-1, and PCL-2 for (a) initial concentration 5 ppm and (b) initial concentration 1.5 ppm (solution volume: 5 mL, polymer mass: 0.08 g, and pH 2).

solution reached a plateau after 30 min of irradiation. This might be because of surface saturation of PCL-2 or occupation of catalyst surface with reduced Cr(III) ions. If there is no contact between TiO_2 and remaining Cr(VI) ions no more reduction occurs. Removal rates were 3.9 ± 0.9% for PCL, 41.8 ± 1% for PCL-1, and 15.5 ± 1% for PCL-2 after 150 min of exposure period in 1.5 ppm concentration. When a UVC lamp emitting 254 nm light was used, the removal rates significantly increased (Fig. 5). The same procedure was also repeated in the presence of citric acid at equivalent concentration of Cr(VI) ions (5 and 1.5 ppm) employing 254 nm UV light. Presence of citric acid slightly improved the adsorption of Cr(VI) ions on polymer (data not given) but greatly enhanced the removal percentages (Fig. 5).

Although removal percentages were lower at 5 ppm initial concentration, TiO_2 immobilized PCL (PCL-1 or PCL-2) was still effective removing almost half of Cr(VI) ions. Especially PCL-1 removed 24.9 ± 1% of Cr(VI) ions after exposure with 365 nm UV light source since no reduction was observed when solution directly exposed to 365 UV nm light. Presence of 254 nm UV light and citric acid had a positive effect on reduction and they increased the removal rate to 48 ± 2% (with PCL-2). This positive effect is possibly due to redox reaction occurred between Cr(VI) ions and citric acid [13] or formation of Cr(VI) ions that forms Cr(V)-citrate complexes [28].

In the case of lower Cr(VI) initial concentration (1.5 ppm), the removal percentages was greatly enhanced. PCL-1 (96 ± 0.9%) or PCL-2 (91 ± 1.1%) removed higher amount of Cr(VI) ions compared to

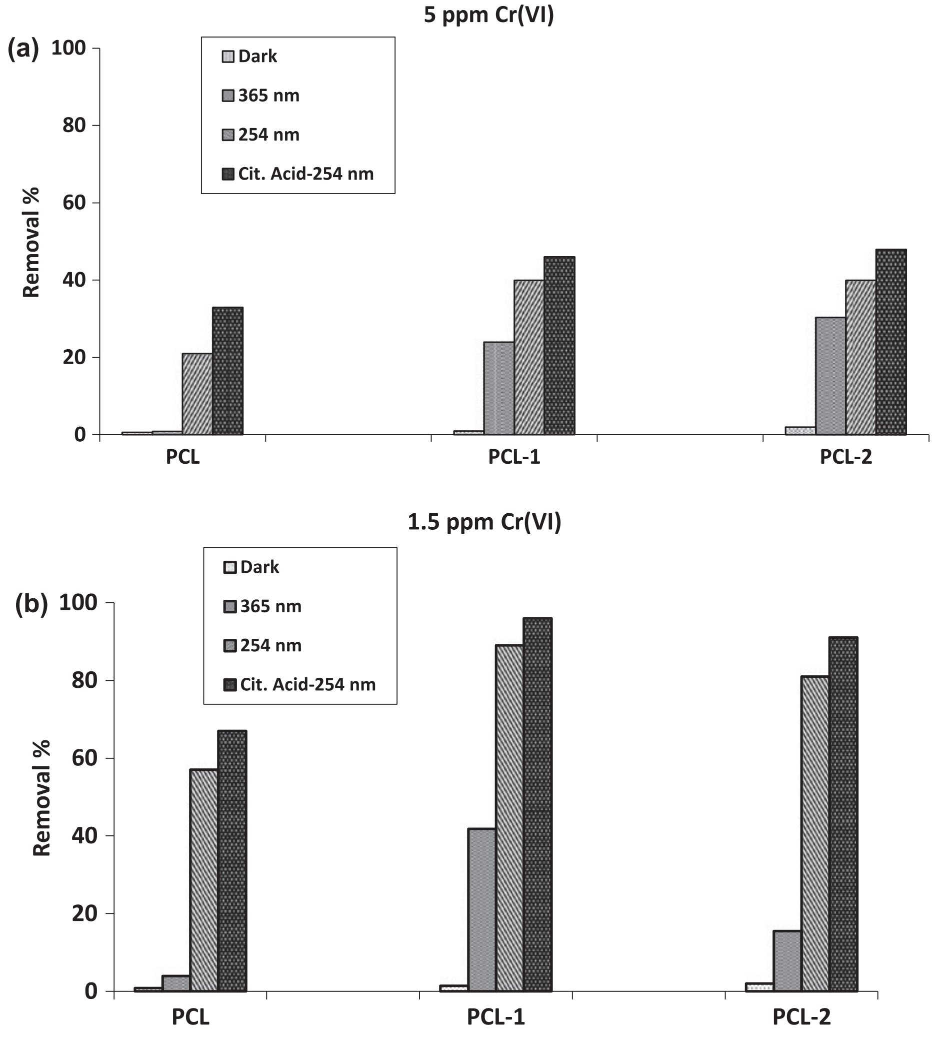

Fig. 5. Removal of Cr(VI) ions after a 150 min exposure (a) 5 ppm and (b) 1.5 ppm (solution volume: 5 mL, polymer mass: 0.08 g, and citric acid concentration equal to initial Cr(VI) concentration).

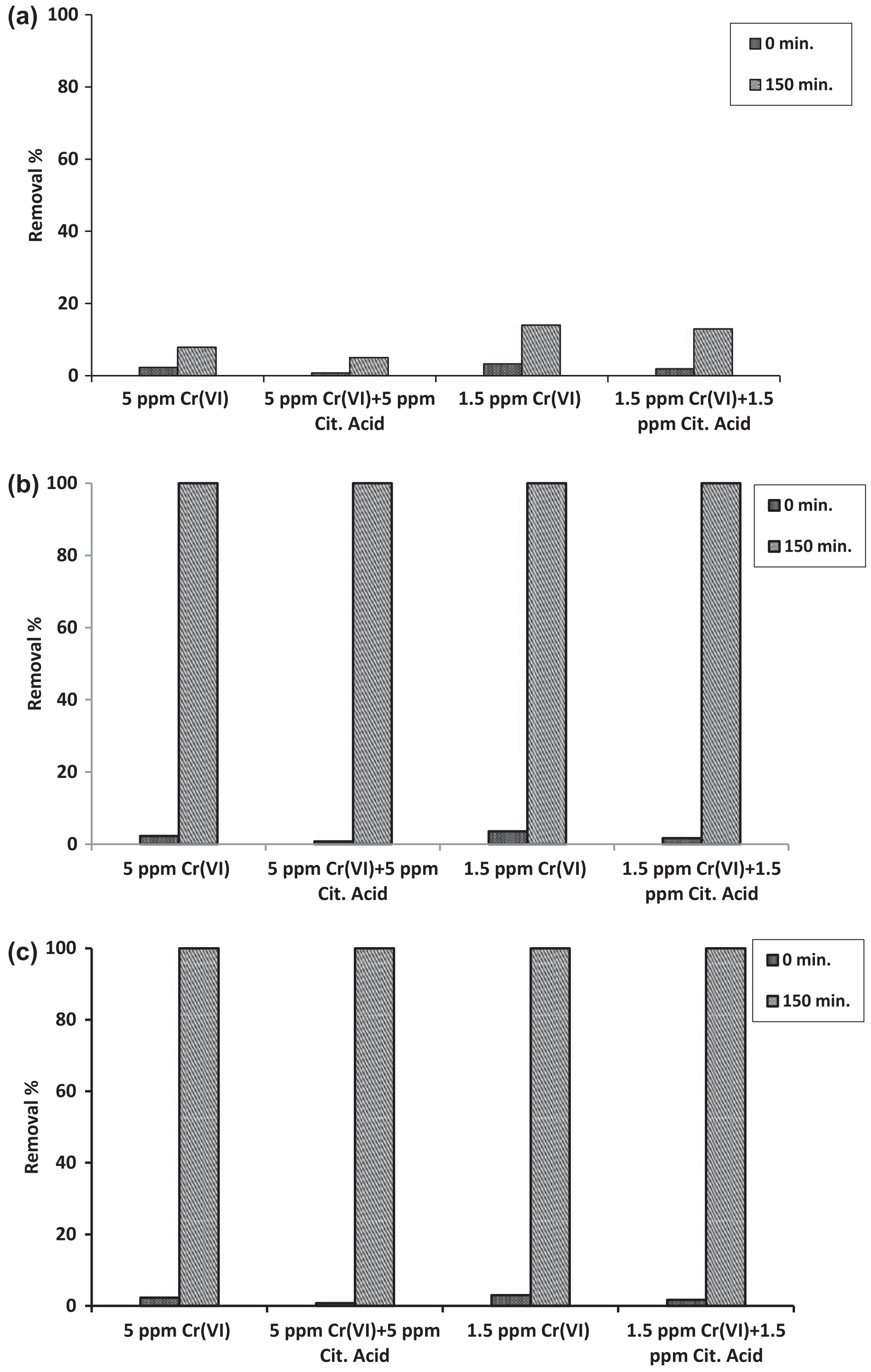

Fig. 6. Removal of Cr(VI) ions treated with neat TiO_2 particles at pH 2 (a) in dark, (b) exposed with 365 nm light, and (c) exposed with 254 nm light (solution volume: 5 mL, TiO_2 mass: 0.004 g, and citric acid concentration is equal to initial Cr (VI) concentration).

PCL alone (57 ± 1%) with 254 nm UV source. It should be noted that when Cr(VI) solution containing neat PCL subjected to UVC exposure (at 254 nm) a remarkable removal was observed for both concentrations. This was considered as interaction of Cr(VI) ions with photolysis products formed from water leading to reduction or Cr(VI) ions and was confirmed by direct photolysis studies and almost 25 ± 2% removal was achieved at 5 ppm Cr(VI) concentration. Direct photolysis produces active species from water leading to oxidation or reduction of target compounds. Cr(VI) ions are possibly reduced by these species similar to photocatalysis but it provides lower transformation rate.

3.2. *Photocatalytic removal of Cr(VI) with neat TiO_2*

Above experiments were carried out with 0.004 g of TiO_2 in suspension in 5 mL of Cr(VI) solution at the same concentrations. In general, TiO_2 itself is a good adsorbent for various inorganic and organic pollutants and an anionic-type adsorption takes place for the adsorption of Cr(VI) ions onto the TiO_2 surface. Therefore, photocatalytic removal of Cr(VI) contains both adsorption of the target ions onto TiO_2 surface and subsequent photocatalytic reduction. The pH at zero point charge (pH_{zpc}) of TiO_2 is 6–7.5 [26] and anionic species of Cr(VI) ions, such as $H_2Cr\,O_4^-$, $H_2CrO_4^-$, and CrO_4^{2-}, are expected to easily be adsorbed onto the positively charged TiO_2 surface below pH 7.5. Removal rates obtained with neat TiO_2 is given in Fig. 6.

As seen from the Fig. 6(a), Cr(VI) ions were not greatly adsorbed on catalyst surface. Presence of citric acid prevents the adsorption of Cr(VI) ions onto TiO_2 particles. Citric acid should be more attractive for absorption onto surface. However, photocatalytic removal percentages were extremely high resulting 100% removal (after 30–150 min illumination either with 365 nm or 254 nm light source). Suspension studies showed that photoreduction is extremely effective in suspension system resulting total removal of Cr(VI) ions. This is expected since TiO_2 and Cr(VI) contact is the highest in suspension system. But after treatment period, the separation of the TiO_2 particles require more labor and energy. However, TiO_2 immobilized PCL is simply removed from the treatment vessel and remaining test solution is quite clear.

3.3. *Reusability TiO_2 immobilized PCL*

More experiments on photocatalytic reduction of Cr(VI) ions were carried out to confirm the reusability of the film with material exhibiting the highest removal rate (PCL-1, 0.08 g, 1.5 ppm Cr(VI), and 254 nm light). The material was washed out with water prior to treatment and kept under 254 nm light for regeneration. This material was reused for photocatalytic reduction experiments and removal percentages were calculated after each treatment (Fig. 7).

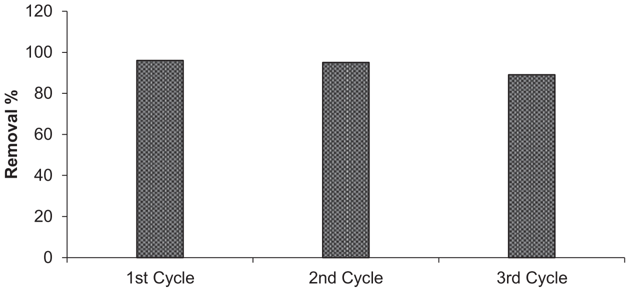

Fig. 7. Reusability tests for PCL-1 (initial concentration 1.5 ppm, solution volume: 5 mL, polymer mass: 0.08 g, pH 2, and 254 nm light).

Similar to first run high removal percentages were obtained for the successive treatments (95 ± 1.5, 89 ± 2% removal after a 150 min illumination, respectively). It means that TiO_2 immobilized material provide repeatable photocatalytic properties and is used for several times after a simple remediation process. On-line column systems employing larger quantity of PCL-1 or PCL-2 is planned for more concentrated solutions.

4. Conclusions

A biodegradable polymer containing n-TiO_2 particles *into* or *onto* PCL was successfully produced with photocatalytical properties. The material successfully removed toxic chromium(VI) ions via photocatalytic reduction from aqueous solution. Especially, TiO_2 immobilized *onto* PCL is effective for removal of Cr(VI) ions and polymer can be easily removed from water after a proper treatment period. Regeneration of the material is simple (needs to be left under UV light for a while) and it can be reused for further treatments. PCL is a safe, nontoxic synthetic polymer which is completely biodegradable when in contact with micro-organisms. It means that after proper removal processes the material can be simply damped into soil and left for total biodegradation.

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